

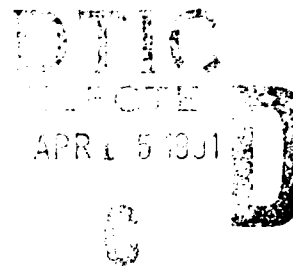


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An Electrochemical Investigation of the 1-Methyl-3-Ethylimidazolium Bromide Aluminum Bromide Molten Salt System

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ABSTRACT

The electrochemical behavior of the room temperature molten salt made by combining 1-methyl-3-ethylimidazolium bromide and aluminum bromide was studied. It was found that the bromide system behaved, for the most part, analogously to the chloride counterpart. Bromide solvated in a room temperature molten salt is electrochemically similar to bromide in other nonaqueous solvent systems. The diffusion coefficients and the heterogeneous rate constants were determined for the bromide and tribromide species in the molten salt.

Although first used more than 40 years ago as an electrolytic bath for plating aluminum (1), room temperature molten salts have received renewed interest in recent years as electrolytes for battery applications. A molten salt electrolyte will theoretically increase the power density of a battery by not only decreasing the weight involved in the electrolyte system but also through the use of new couples which become feasible in a molten salt system.

We have described previously a battery cell that employs a rechargeable bromine-bromide electrochemical couple in the 1-methyl-3-ethylimidazolium chloride-aluminum chloride low-temperature molten salt (2). Preliminary experiments show that the electrochemistry of the bromine-bromide couple is complex, possibly due to halide exchange in the chloroaluminate melt. We report here a detailed electrochemical study of bromine and bromide in the chemically similar 1-methyl-3-ethylimidazolium bromide-aluminum bromide system.

Although Popov and Geske (3), among others, have characterized the nonaqueous electrochemical behavior of the different bromide-containing species, the chemical and electrochemical properties of the room temperature molten salts are different enough to warrant the investigation of bromide when it is solvated in the melt system.

Experimental

1-methyl-3-ethylimidazolium chloride (MEIC).—The MEIC was prepared by a method similar to that presented by Wilkes *et al.* (4). The procedure was changed to eliminate the high pressures involved in the reaction vessel by

running the reaction at a lower temperature (ca. 30°C) for a longer time (ca. 2 weeks). The purity of the MEIC was confirmed by noting the lack of any unreacted 1-methylimidazole in the MEIC by ¹H NMR, and by noting the absence of the electrochemical reduction of any protonic impurity in a melt prepared from the MEIC.

1-methyl-3-ethylimidazolium bromide (MEIB).—The MEIB was prepared by a method similar to that described by Sanders *et al.* (5, 6). The only modifications was that the reaction was carried out in a round bottom flask with a reflux condenser attached. The reaction mixture was heated to keep the ethyl bromide refluxing. The purity of the MEIB was checked in a manner similar to that of the MEIC.

Aluminum bromide.—The aluminum bromide (Aldrich, 98+%) was purified by vacuum sublimation. The aluminum bromide was repeatedly sublimed until no color was observed in the collected material (a total of 3-5 sublimations).

Aluminum chloride.—The aluminum chloride was purified by the method described by Wilkes *et al.* (7).

Tetramethylammonium tribromide.—The tetramethylammonium tribromide was prepared by the method described by Chattaway and Hoyle (8) and characterized by UV-VIS spectroscopy as described by Buckles *et al.* (9).

The electrochemistry was carried out in a Vacuum Atmospheres Company dry box with a combined H₂O/O₂ concentration of less than 10 ppm. The atmosphere in the dry box was UHP helium purified by a Vacuum Atmospheres MO-40 Dri-Train. The quality of the atmosphere

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was continually monitored by a light bulb whose filament was exposed to the dry box atmosphere.

All electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a Model 179 Digital Coulometer plug-in module. Any required potential or current programming was provided by a PAR Model 175 Universal Programmer. The potentials were monitored with a DANA Model 5330 digital voltmeter. The electrode used in these experiments was a platinum disk, 6 mm diam, imbedded in a Teflon sleeve, purchased from Pine Instruments Company. Rotation of the working electrodes was accomplished with a Pine Instruments Company MSR electrode rotator.

The reference electrode currently used in our lab is made observing the $\text{Al}^{3+}/\text{Al}^0$ couple formed by placing an aluminum wire in an $N = 0.600$ chloride melt, with an asbestos fiber separating the reference electrode from the working compartment of the cell. To investigate the possible interferences due to the chloride migration across the reference electrode junction into the bromide melt, a cell was constructed with a chloride reference electrode and a neutral bromide melt. A cyclic voltammogram was obtained on the cell immediately after construction and, again, after six days of continuous contact between the chloride electrode and the bromide melt. No effect of the migration of the chloride ion across the junction was observed at the current limits with which we were interested. Because of the negligible effect of the chloride ions crossing the reference electrode junction and the long-term instability of the bromide melts, we used the chloride reference electrode throughout this work.

Scans taken at less than a volt per second were recorded on a Houston Instruments Model 2000 Omnigraphic X-Y recorder. Scans taken at greater than 1 V/s were recorded on a Nicolet Model 204A storage oscilloscope and then plotted on the Omnigraphic recorder. Cell heating was performed by a resistive block heater. The temperatures were monitored by a Doric Model 412A Trendicator, using a type K thermocouple.

Sanders and Hussey (5, 6, 10) determined the physical properties of the AlBr_3 -MEIB melts used throughout this work. The physical properties are similar to those of the chloride system; but the melting points of the bromide system are approximately 50° higher than the chloride.

The same definitions which are used for the chloroaluminate molten salt systems were used in this work. Since there is no unreacted aluminum bromide present in the melt, upon completion of the dissolution reactions the term N is used to indicate the apparent mole fraction of aluminum bromide present in the binary melt. As with the chloride system, the experimental working range of N was limited to the region between $N = 0.333$ and $N = 0.667$ because of the higher temperatures required to make a homogeneous melt outside of this range.

The stoichiometry of the molten salt determines its anionic composition, which is shown as a function of the apparent mole fraction of aluminum bromide in Fig. 1.

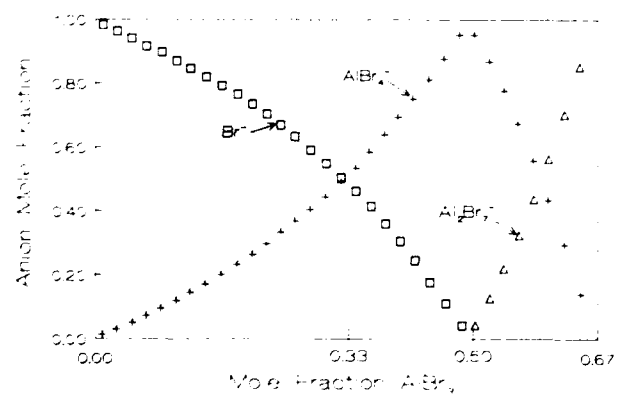
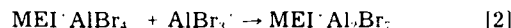


Fig. 1. Anionic composition diagram for the bromoaluminate molten salt system.

Raman spectroscopic studies (11) indicate that Al_2Br_7^- and AlBr_4^- exist in bromoaluminate melts in an analogous fashion to Al_2Cl_7^- and AlCl_4^- in chloroaluminate melts. The dissolution reactions for the MEIB- AlBr_3 melts are thus



Because of the presence of bromide, which acts as a Lewis base, any melt with N less than 0.5 is referred to as a basic melt. Heptabromoaluminate (Al_2Br_7^-) acts as a Lewis acid so any melt with an N greater than 0.5 is termed acidic. Because of the lack of the Lewis base (bromide) and the Lewis acid (heptabromoaluminate), a melt with N equal to 0.5 is called a neutral melt.

Results and Discussion

It was found that, unlike the chloride system, the formation reactions (Eq. [1] and [2]) of the bromoaluminate melts are appreciably slow. It was also found that bromide melts tend to turn the distinctive orange-brown color associated with bromine. This coloration is probably due to the oxidation of the bromide. In order to ensure the completion of the dissolution reactions, once a melt was made, it was allowed to stand at 60°C for at least 12h prior to use. The melt was then used for no longer than three days before being destroyed, in order to minimize any effects of changes in the melt composition.

Figure 2 shows the cyclic voltammogram of an $N = 0.490$ bromide melt at glassy carbon, tungsten, and platinum electrodes. Because of the apparent high degree of electrochemical irreversibility of the oxidative processes on the other electrodes, platinum was chosen as the working electrode material for the rest of this work.

Some workers (5, 10) have worked with the bromide melts assuming the melts behave the same as the chloride counterparts. This work initially made, but then verified this assumption. To gain an initial understanding of the electrochemistry involved in the bromide system, cyclic voltammograms of an acidic, basic, and neutral melt were obtained.

Neutral melt.—The cyclic voltammogram of a neutral bromide and a neutral chloride melt are shown in Fig. 3. If the initial assumption is correct, the only species present in the neutral bromoaluminate molten salt are the tetrabromoaluminate anion and the imidazolium cation. The cathodic limit of the melt is the irreversible reduction of the imidazolium cation and is approximately the same for

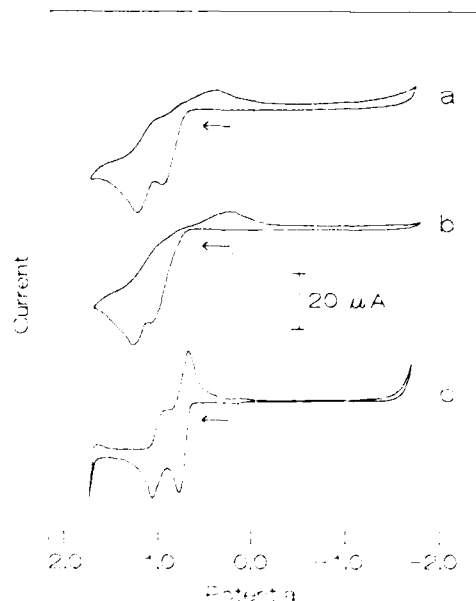


Fig. 2. Cyclic voltammogram of an $N = 0.490$ bromide melt at a (a) glassy carbon, (b) tungsten, and (c) platinum electrode.

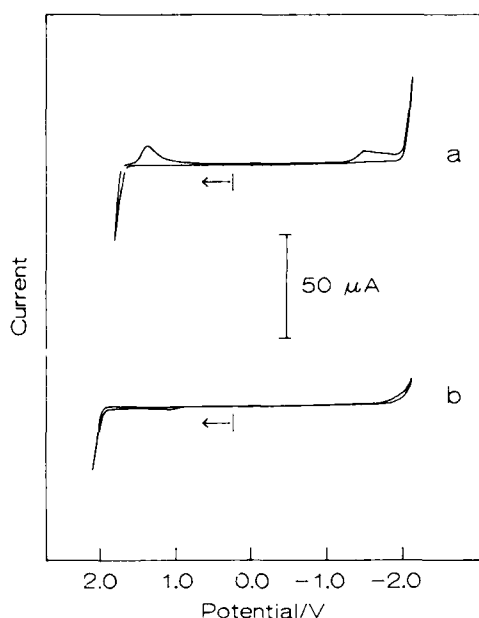
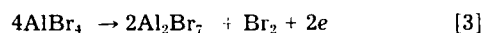


Fig. 3. Cyclic voltammogram of a neutral (a) bromide and (b) chloride melt.

the chloride and bromide melts. The anodic limit of the melt is the oxidation of the tetrabromoaluminate by the half reaction



Even though there are no redox couples observed between the melt limits, when the potential is swept slowly, if the potential is swept into the anodic region quickly, a deposition and stripping wave is seen which is similar to that seen in an acidic melt. These observations argue for the validity of the initial assumption that the neutral bromide and chloride melts are analogous to one another.

Acidic melts.—Upon the addition of a small amount of aluminum bromide to the neutral melt, the melt becomes slightly acidic (resulting in a small concentration of the heptabromoaluminate anion). The cyclic voltammograms of a slightly acidic ($N = 0.510$) bromide and chloride melt are shown in Fig. 4. The half reactions which determine

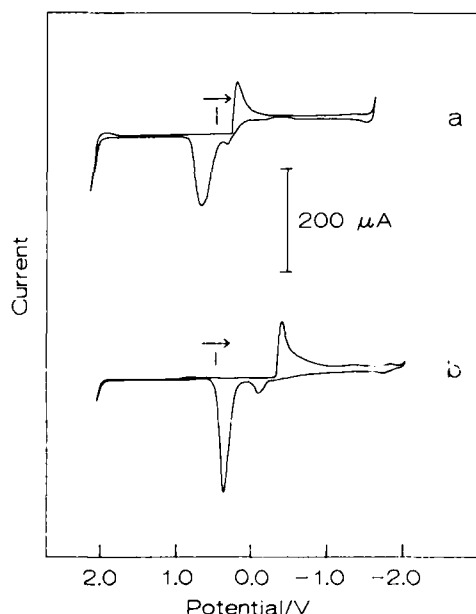


Fig. 4. Cyclic voltammogram of a slightly acidic ($N = 0.510$) (a) bromide and (b) chloride melt.

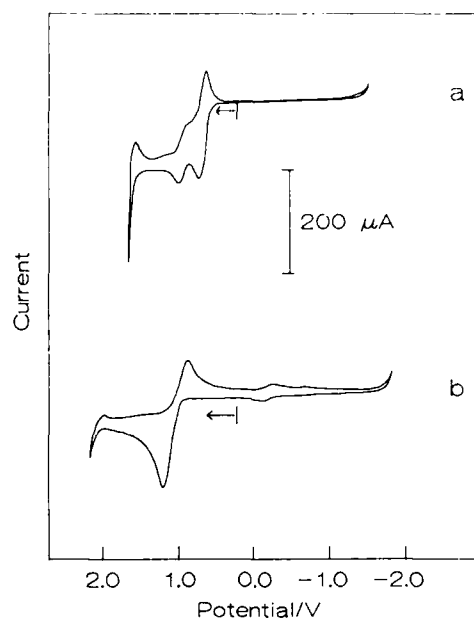
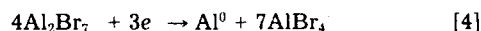


Fig. 5. Cyclic voltammogram of a slightly basic ($N = 0.490$) (a) bromide and (b) chloride melt.

the potential limits of the melt remain the same as those of the neutral melt, but now there is a reduction due to the heptabromoaluminate anion. The magnitude of the reductive process increases from 0 in the neutral melt, as the apparent mole fraction of aluminum bromide increases.

The sharp break at the start of the reduction peak is commonly seen in nucleation phenomena preceding a deposition process. The non $t^{1/2}$ decay seen on the related oxidation wave is indicative of an insoluble species being stripped off of the electrode surface. The half reaction for this reductive process is



The voltammogram in Fig. 4 demonstrates that, in general, the analogy between the bromoaluminate and chloroaluminate melts holds up well with respect to the behavior of acidic species in the bromoaluminate melts.

Basic melts.—Upon the addition of a small amount of MEIB to a neutral melt, the melt becomes slightly basic and a small concentration of bromide results. The cyclic voltammograms of an $N = 0.490$ bromide and chloride melt are shown in Fig. 5. Unlike the chloride system, the bromide system shows two electrochemical processes for the oxidation of the bromide. A major focus of this work was to assign and characterize these two oxidative processes.

As is common, the formal electrode potentials of the two oxidative processes in the basic bromide system were determined from the cyclic voltammograms by the method described by Kissinger and Heineman (12). The formal electrode potential of the first oxidative process was found to be independent of the rate at which the electrode potential was scanned and is 0.684V vs. the $\text{Al}^{3+}/\text{Al}^0$ reference electrode described earlier. The second oxidative process

Table I. Transfer coefficients and number of electrons transferred

Technique	Wave 1		Wave 2	
	α	n	α	n
RDLSV	0.41	1	0.54	1
LSV	^a	1	^a	^a
Amperometry	0.55	1	^a	^a
Coulometry			1.0 ^b	

^a Could not be determined due to the proximity of the two waves.

^b Overall number of electrons transferred for the combined first and second oxidative processes.

Table II. Diffusion coefficients and Stokes-Einstein products of different species solvated in molten salts and acetonitrile

Species	Melt		Acetonitrile	
	$D/\text{cm}^2 \text{ s}^{-1}$	$\frac{D\eta}{T}/\text{g cm s}^{-2} \text{ K}^{-1}$	$D/\text{cm}^2 \text{ s}^{-1}$	$\frac{D\eta}{T}/\text{g cm s}^{-2} \text{ K}^{-1}$
Br	7.4×10^{-7}	2.5×10^{-10}	1.2×10^{-5}	1.6×10^{-10}
Br ₃	9.4×10^{-6}	3.2×10^{-9}	2.0×10^{-5}	2.7×10^{-10}
Cl	9.6×10^{-7}	4.9×10^{-10}	2.4×10^{-5}	2.8×10^{-10}

was found to be dependent on the scan rate. The formal electrode potential as a function of the square root of the scan rate was extrapolated to a scan rate of zero. The resulting formal electrode potential is 1.01V vs. the Al³⁺/Al⁰ reference.

The number of electrons transferred, n , and the transfer coefficients, α , were determined for each of the two oxidative processes by variety of electrochemical techniques. The product αn was determined using rotating disk linear sweep voltammetry and stationary electrode linear sweep voltammetry based on the slope of the leading edge of the voltammetric wave. The αn product was also calculated using constant current amperometry and the linear portion of the resulting Allen-Hickling plots. Under the assumption that quasireversible reactions have a transfer coefficient near 0.5 allows the assignment of $n = 1$ for each of the two oxidation processes. The number of electrons was determined for the overall oxidation process by carrying out exhaustive oxidation of bromide, present in a slightly basic melt, at a potential anodic of the second oxidative process. The value of n for the overall process is 1.0. The proximity of the two oxidation waves precluded the use of coulometry in determining the number of electrons involved with the individual oxidation processes.

Table I shows a summary of results for the number of electrons and transfer coefficients for the oxidation processes.

Finally, tribromide in the form of tetramethylammonium tribromide was added to an $N = 0.490$ bromide melt. The cyclic voltammograms of the melt run before and after the addition of the tribromide are shown in Fig. 6. Although the technique is not a definitive proof of the identity of the species being oxidized, it strongly supports the assignment of the tribromide anion to the second oxidative process. The addition of known tribromide also clarifies the reductive process. The anodic peak at 1.1V and the cathodic peak at 0.7V greatly increase, thus sub-

stantiating that tribromide is both oxidized and reduced during the voltammetry.

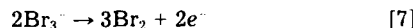
The assignments proposed by Popov and Geske (3) for the oxidation of bromide in other nonaqueous electrolytes apply, also, to the molten salt electrolyte. The first anodic process is the oxidation of the bromide to bromine by the half reaction



after which the resulting bromine undergoes a chemical reaction with the remaining bromide to form the tribromide anion



The second anodic process is the oxidation of the tribromide by the half reaction



The diffusion coefficients of the bromide and tribromide anions were determined by rotating disk linear sweep voltammetry. The values determined for the diffusion coefficients and the corresponding Stokes-Einstein products are listed in Table II along with the literature values determined by Iwasita and Giordano (13) in acetonitrile. Also listed in Table II are the values for the diffusion of chloride through a chloride melt (14) and acetonitrile as determined by Serano *et al.* (15). The lower values of the diffusion coefficients in the molten salts compared to in acetonitrile are generally explained by the high viscosities of the molten salts.

These results support the model of a highly organized crystal structure in the melts, which has been reported previously by our laboratory (16). The higher diffusion coefficient for the tribromide, compared to the bromide and chloride, is puzzling at first glance. The explanation probably lies in the fact that chloride (and probably bromide) hydrogen bonds to the organic cation to a greater extent than the tribromide.

The heterogeneous rate constants were determined for the bromide and the tribromide ions by the peak separation method of Nicholson (17) and are shown in Table III. The magnitude of the rate constant (10^{-2} - 10^{-3}) indicates that there is an appreciable degree of electrochemical irreversibility for these two processes, even at the platinum electrode.

Conclusion

The oxidation of bromide in the low-temperature bromoaluminate melts is more complex than chloride oxidation in the similar chloroaluminate melts. The two-step electrochemical oxidation is similar to that seen in acetonitrile.

The electrochemical oxidation occurs in two steps involving tribromide ion, similar to the processes observed in other nonaqueous solvents. Otherwise, the melts behave similarly to the analogous chloroaluminate system.

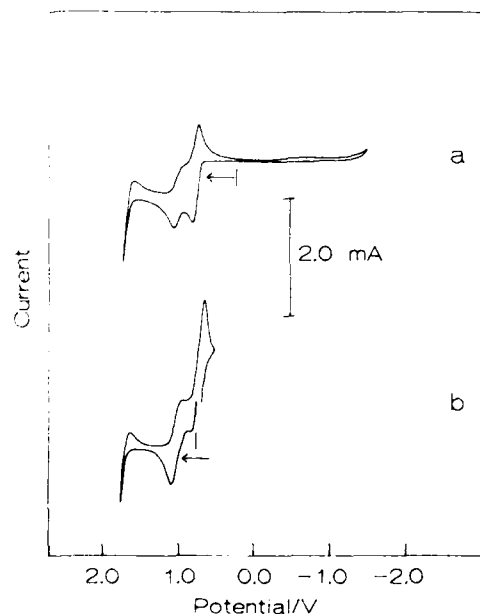


Fig. 6. Cyclic voltammogram of an $N = 0.490$ bromide melt (a) before and (b) after the addition of tetramethylammonium tribromide.

Table III. Heterogeneous rate constant as a function of sweep rate

$v/\text{mV/s}$	Wave 1		Wave 2	
	$\Delta E_p/\text{mV}$	$k^0/\text{cm/s} \times 10^3$	$\Delta E_p/\text{mV}$	$k^0/\text{cm/s} \times 10^3$
50	77	2.78 ± 0.68	86	6.56 ± 1.04
100	81	3.30 ± 0.71	107	4.87 ± 0.71
200	96	2.68 ± 0.42	79	17.6 ± 3.5
500	117	2.38 ± 0.22	94	16.0 ± 2.6

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